



ON THE TEACHING OF THE DIFFERENT FORMULATIONS OF THE VIRIAL EQUATION

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ABSTRACT

Chemistry educators teaching chapters on "real gases" usually present to the students the "virial development" of Kamerlingh Onnes for the equation of state, which takes into account interactions of the molecules in aggregates by a successive series of parameters (B , C , etc.), yielding a polynomial equation on the concentration (equivalent to the inverse of the molar volume). A well known transformation of the virial equation to a polynomial equation as a function of pressure is also widely used, with suitable coefficients (B' , C' , etc.). The literature presents relationships between the second and third virial coefficients for both equations, for example $B' = B/RT$. Students usually assume that both formulations should deliver to similar calculated results. However, when using the relationships mentioned above to perform calculations for the same gas conditions of pressure and temperature, discrepancies are observed in the molar volume obtained by the two formulations of the virial equation. Chemistry educators are required to present such discrepancies, explain them and interpret them. In addition to that, a possible alternative practical approach is to develop a relationship between the second virial coefficients B and B' , that yields suitable results when using both formulations.

KEYWORDS: Upper Division Undergraduate, Physical Chemistry, Gases, Virial Equation.

The "virial expansion" is considered one of the most interesting and versatile equations of state for gases (Salzman, 2004). It was developed by Kamerlingh Onnes at the end of the 19th century as an improvement of the van der Waals equation, based on the law of corresponding states (Wisniak, 2003), and it is used almost in every Physical Chemistry course as one of the possible tools describing behavior of "real" gases. The virial expansion is a power series in powers of concentration, and has the general form:

$$P = cRT(1 + Bc + Cc^2 + \dots) = \frac{RT}{V_m} \left[1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \dots \right] \quad (1)$$

where P is the pressure, c the molar concentration, R the gas constant, T the absolute temperature, B and C the second and third virial coefficients, respectively, and V_m the molar volume, defined as the reciprocal of the concentration, thus $V_m = 1/c = V/n$, where V is the volume and n the amount of moles. The successive virial coefficients B , C , etc. take into account deviations from the ideal gas law due to interaction of the molecules in pairs, triplets, etc (Riddell & Uhlenbeck, 1953).

The virial equation truncated at the second coefficient is considered a relatively simple, yet accurate method for describing the state of gases, even at relatively high pressures (Hayden & O'Connell, 1975). Considering several presented theoretical and empirical methods to evaluate the second virial coefficient (Dymond, Cholinski, Szafranski, & Wyrzykowska-Stankiewicz, 1986; Hayden & O'Connell, 1975; O'Connell & Prausnitz, 1967; Pitzer & Curl, 1957; Riddell & Uhlenbeck, 1953; Tsonopoulos, 1974), a useful equation of state for low or moderate vapor densities may be based on determination of the required B parameter: when the temperature and the molar volume are known, the pressure might be evaluated using:

$$Z = \frac{PV_m}{RT} = \left[1 + \frac{B}{V_m} \right] \quad (2)$$

where Z is the "compressibility" or "compression factor", which is a useful measure of the deviation of a real gas from an ideal gas. For an ideal gas, the compression factor is equal to 1 (Atkins & de Paula, 2006; Salzman, 2004). If the pressure is known, V_m can also be evaluated by transforming Eq. (2) and solving a quadratic equation. However, where the molar volume is to be determined, an alternate form of the virial equation is usually presented as (Atkins & de Paula, 2006):

$$\frac{PV_m}{RT} = (1 + B'P + C'P^2 + \dots) \quad (3)$$

which, when considering only the second virial coefficient yields:

$$Z = \frac{PV_m}{RT} = (1 + B'P) \quad (4)$$

B' and C' are also known as virial coefficients. The relationship between these parameters and the "original" virial coefficients is usually denoted as (Atkins & de Paula, 2006; Boschi-Filho & Butters, 1997; Salzman, 2004):

$$B' = \frac{B}{RT}, \quad C' = \frac{C - B^2}{(RT)^2} \quad (5)$$

Students usually will assume that by using the truncated virial equation (Eqs. [2], [4]), as is commonly done (Hayden & O'Connell, 1975; O'Connell & Prausnitz, 1967; Pitzer & Curl, 1957), combined with the relationships presented in Eq. [5] should deliver the same P , V and T values. However, it is the duty of the Chemistry Educators to point out that in fact this practice yields inconsistencies in the evaluated values. For example, for CO_2 at 280K, $B = -0.146 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ (Kehiaian, 2005). Evaluating the molar volume of CO_2 at 280K with a pressure of 2 MPa by transforming Eq. (2) into a quadratic equation and solving for V_m yields $0.9926 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$, and $Z = 0.853$. On the other hand, calculation of $B' = -6.354 \times 10^{-8} \text{ Pa}^{-1}$ using Eq. [5] followed by Eq. (4) yields $V_m = 1.018 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ and $Z = 0.875$ —a discrepancy of about 3%. Discrepancies increase considerably with pressure, and at 3.5 MPa, differences exceed 15%, with Z values of 0.675 and 0.780 for Eqs. (2) and (4), respectively.

The use of the less truncated equation, including the third virial coefficient considerably improves the fit between the two formulations, but even then, discrepancies remain: for example, very detailed values of B and C are given by Estrada-Alexanders and co-workers from the integration of speed of sound (Estrada-Alexanders, Guzmán, & Pérez-Vidal, 2012). For CO_2 at 280K they report $B = -0.1421 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$ and $C = 5.278 \times 10^{-9} \text{ m}^6 \text{ mol}^{-2}$. By using Eq (5), values of $B' = -6.105 \times 10^{-8} \text{ Pa}^{-1}$ and $C' = -2.754 \times 10^{-15} \text{ Pa}^{-2}$ are obtained. At a pressure of 3.5 MPa, V_m and Z values are $(0.4586 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}, 0.715)$ and $(0.4759 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}, 0.742)$ using Eqs. (1) or (3), respectively, a close to 4% discrepancy.

A detailed examination focusing on the truncated equation shows that such discrepancies are indeed inherent: combination of Eqs. [2] and [4] delivers two different definitions for the compressibility that should converge:

$$Z = \frac{V_m P}{RT} = (1 + B'P) = \left(1 + \frac{B}{V_m} \right) \quad (6)$$

However, introducing the commonly used relationship between B and B' (Eq.(5)) yields:

$$\begin{aligned} \left(1 + \frac{B}{RT} P \right) &= \left[1 + \frac{B}{V_m} \right] \\ \left(\frac{B}{RT} P \right) &= \left[\frac{B}{V_m} \right] \\ P V_m &= RT \end{aligned} \quad (7)$$

presumably indicating that the gas behaves according to the perfect gas equation of state, with $Z = 1.00$.

The discrepancy between the "reality" (P, V, and T of the actual gas) and the mathematical models developed to describe such reality should be elaborated in front of the students. G.E.P. Box (Box, 1976) explains that "In applying mathematics to subjects such as physics or statistics we make tentative assumptions about the real world which we know are false but which we believe may be useful nonetheless".

For students seeking a coherent model that can yield the same calculated results for both Eqs. [2] and [4], an alternative to Eq. [5] can be developed, yielding a different relationship between both "second virial coefficients". Reorganizing Eq. (6) leads to:

$$B' = \left[\frac{B}{PV_m} \right] = \frac{B}{RT(1 + B'P)} = \frac{B}{RT \left(1 + \frac{B}{V_m} \right)} \quad (8)$$

where the definition of B' as a function of V_m can be readily used if the molar volume is known. When pressure is the known value, as in the examples given above, Eq. (8) can be elaborated to isolate B' to $B' + B'^2 P = \frac{B}{RT}$ which can then be easily solved as a quadratic equation.

Using this approach on the example presented above, and calculating the molar volume of CO_2 at $P = 2 \text{ MPa}$ and $T = 280\text{K}$, leads to $B' = -7.353 \times 10^{-8} \text{ Pa}^{-1}$, and the use of Eq. [4] yields $V_m = 0.9926 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$, and $Z = 0.853$, exactly the same results as from Eq. [2]. The same happens for $P = 3.5 \text{ MPa}$: $B' = -9.298 \times 10^{-8} \text{ Pa}^{-1}$ and $V_m = 0.4486 \times 10^{-3} \text{ m}^3 \text{ mol}^{-1}$, $Z = 0.675$ for both methods of calculation.

Thus, by evaluating B' using the relationship presented herein, consistent results of the two formulations of the virial equation are achieved. However, students (and educators as well) might recall that this is only a model, and "Since all models are wrong the scientist cannot obtain a 'correct' one by excessive elaboration." (Box, 1976).

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